Facile Functionalization of a Metal Carbon Bond by O-Atom Transfer

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General Considerations: All air and water sensitive procedures were carried out either in a MBraun inert atmosphere glove box under N_2, or using standard Schlenk techniques under argon. Pyridine oxide was purified by sublimation. Labeled reagents $H_2{}^{18}O$ (Cambridge Isotopes) and $CH_3{}^{18}OH$ (Sigma-Aldrich) were used as purchased. Methyltrioxorhenium was purchased from Strem . GC/MS analysis was performed on a Shimadzu GC-MS QP5000 (ver. 2) equipped with cross-linked methyl silicone gum capillary column (DB5). The retention times of the products were confirmed by comparison to authentic samples. NMR spectra were obtained on a Varian Mercury-400 spectrometer at room temperature. All chemical shifts are reported in units of ppm and referenced to the residual protonated solvent.

Oxygen labeling: ^{16}O-MTO + $I^{18}O_4^-$ ⟶ $CH_3{}^{18}OH$: 50.5 mg $NaIO_4$ (2eq) were added to 0.5 mL $H_2{}^{18}O$ and allowed to equilibrate for 30 minutes at room temperature with sonication (the exchange of ^{16}O for ^{18}O under such conditions is extremely fast[1]). 25.2 mg MTO were added directly to this solution. The reaction quickly turned yellow, then clear within one minute of addition. The reaction mixture was allowed to sit at room temperature for 10 minutes. 1μL was analyzed by GC/MS for methanol content. The fragmentation pattern of methanol produced from the reaction was compared to patterns for $CH_3{}^{18}OH$ and $CH_3{}^{16}OH$. Appearance and relative intensities of peaks in the fragmentation pattern matched that of $CH_3{}^{18}OH$. No evidence of $CH_3{}^{16}OH$ was present by comparison of the fragmentation pattern to known mixtures of $CH_3{}^{18}OH$ and $CH_3{}^{16}OH$. The rate of ^{18}O incorporation into MTO was slow relative to the incorporation into IO_4^- and the production of methanol as measured by GC/MS.

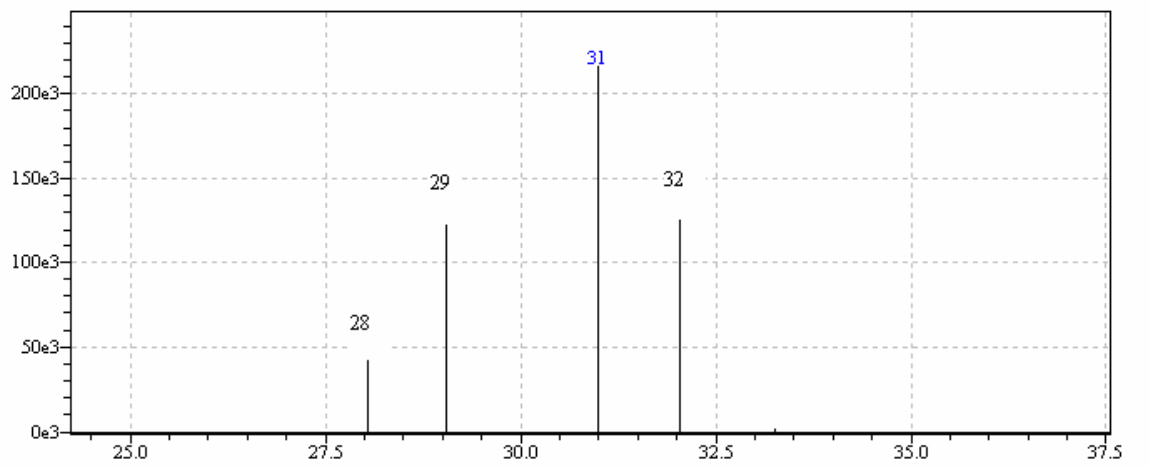

Figure 1: Fragmentation pattern for $CH_3{}^{16}OH$ in H_2O (absolute intensity vs. m/z).

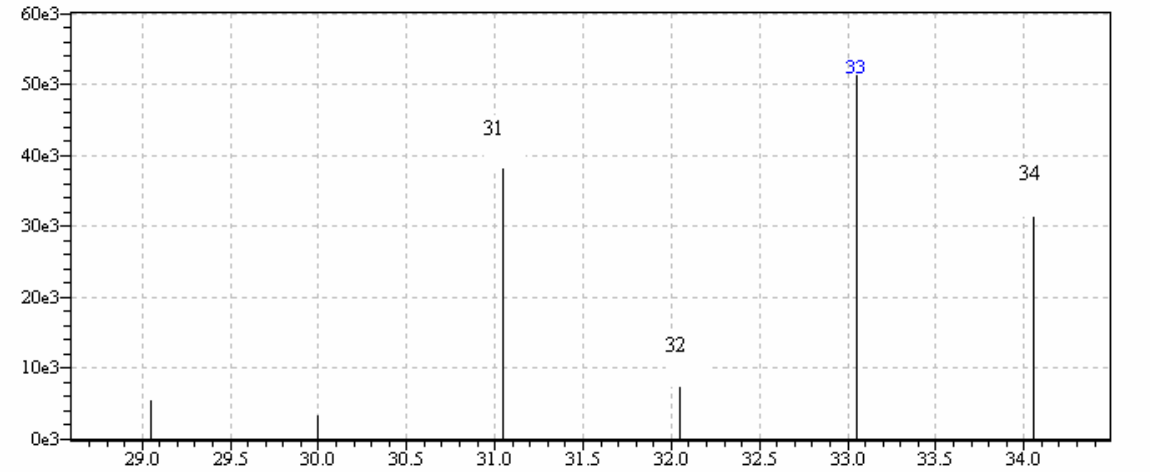

Figure 2: Fragmentation pattern for $CH_3{}^{18}OH$ in H_2O (absolute intensity vs. m/z).

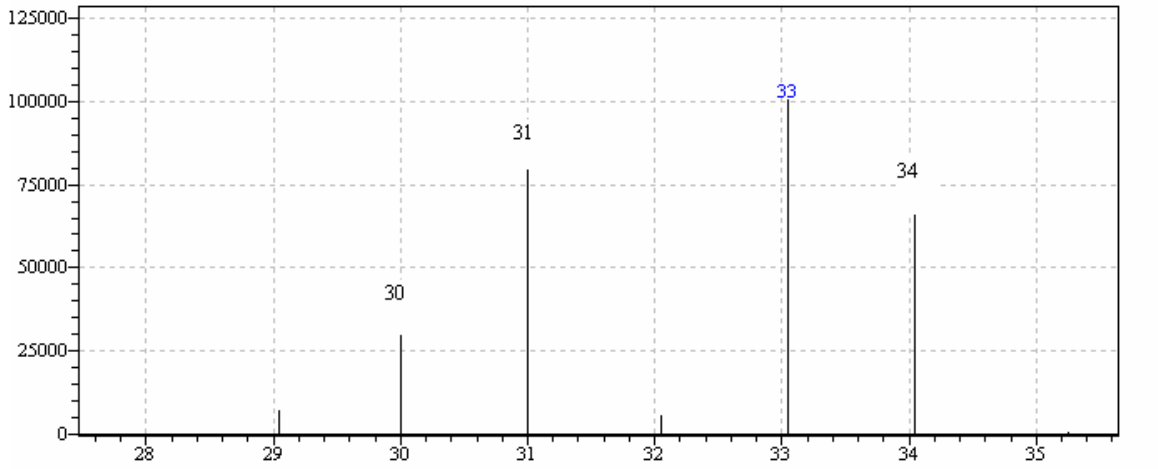

Figure 3: Fragmentation pattern for $CH_3{}^{18}OH$ from MTO + $NaI^{18}O_4$ reaction in $H_2{}^{18}O$ (absolute intensity vs. m/z).

^{18}O-MTO labeling: ^{16}O-MTO + $H_2{}^{18}O$: To verify that the incorporation of ^{18}O into MTO was slow compared to the incorporation into the oxidant, IO_4^-, we studied this reaction by GC/MS. 28.5 mg MTO was dried thoroughly in vacuo inside a flame dried schlenk tube, sealed with a Chemglass Teflon valve. 1g $H_2{}^{18}O$ was added using standard schlenk technique. The solution was sonicated for 90 minutes to increase the solubility of MTO in solution and promote the incorporation of ^{18}O. The solution was analyzed by GC/MS at this point and the fragmentation pattern compared to the blank (^{16}MTO in H_2O). The solution was then sonicated for 45 minutes and analyzed again by GC/MS. Though the rate of incorporation was not explicitly measured, as this would require deconvolution due to the natural abundance of Re isotopes (^{187}Re: 62.60%, ^{185}Re: 37.4%) it is clear from the fragmentation intensities that incorporation is slow relative to the instantaneous reaction of $H_2{}^{18}O$ with IO_4^- at room temperature. Ignoring the m/z=248 and 250 peaks as possibly having no incorporation (of course m/z=250 *may* have one ^{18}O swapped for a ^{16}O atom), one concludes that the lower limit of incorporation at 135 minutes is 57.9% based on fragmentation intensities.

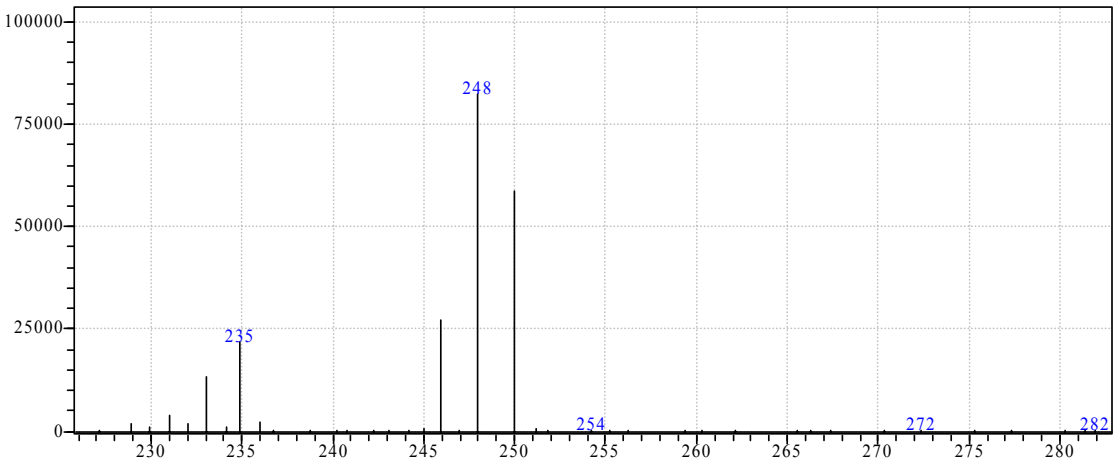

Figure 4: Control. Fragmentation pattern of ^{16}O-MTO in $H_2{}^{16}O$ (absolute intensity vs. m/z).

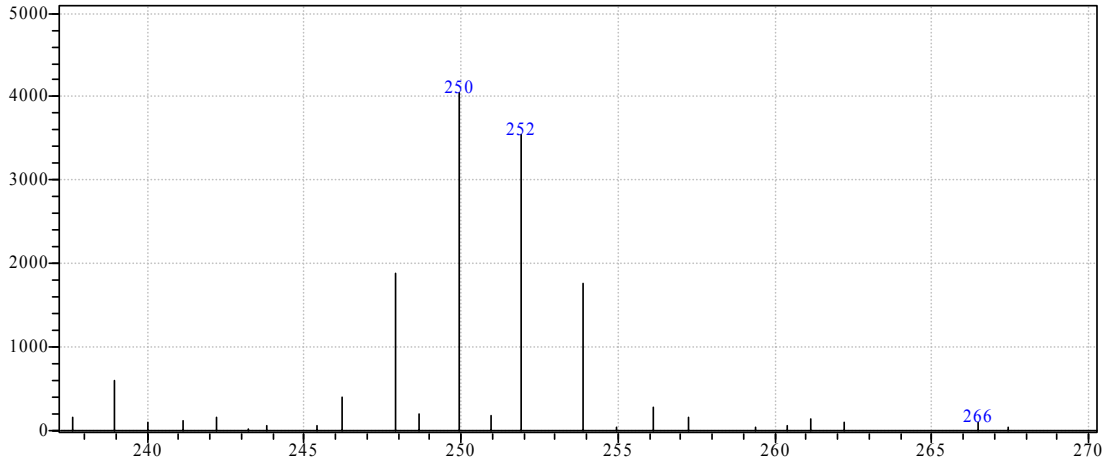

Figure 5: Fragmentation pattern of ^{16}O-MTO in $H_2{}^{18}O$ after 90 minutes(absolute intensity vs. m/z).

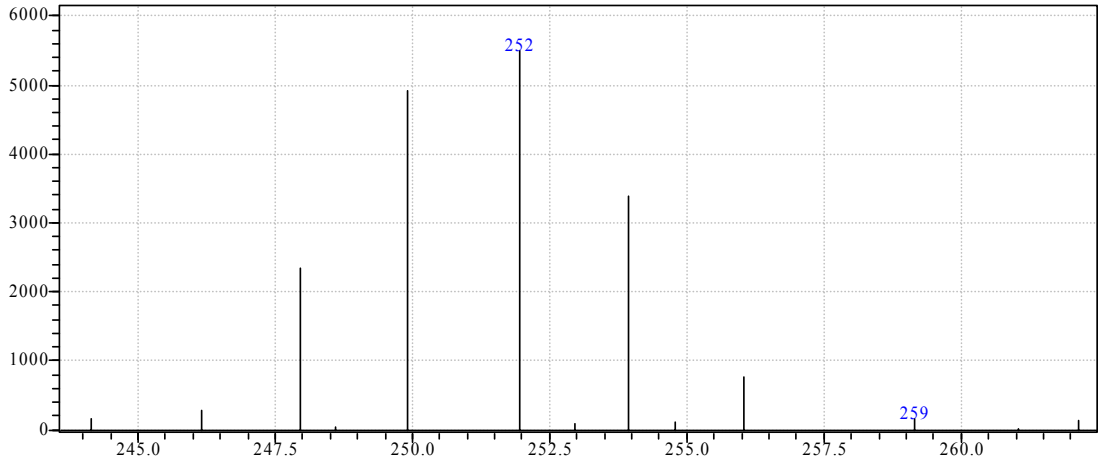

Figure 6: Fragmentation pattern of ^{16}O-MTO in $H_2{}^{18}O$ after 135 minutes (absolute intensity vs. m/z).

$(CH_3)ReO_3(py)$ + pyO ⟶ CH_3O-$ReO_3(py)$: 12.0mg MTO were dissolved in 155µL $pyridine_{d5}$. To this solution was added 0.40mL THF_{d8}, 9.2mg pyO (2eq), and co-axial capillary containing cyclohexane internal standard (3.2µL cyclohexane in 50µL CCl_4). The ^1H NMR was taken at this point (t=0). The solution was heated at 125°C for 1h. The solution turned orange and precipitated an orange solid on the walls of the J-Young tube. A yield of 40% was calculated based on conversion of MTO to methoxide, though this does not take into account the precipitated product. No other products were detected by NMR.

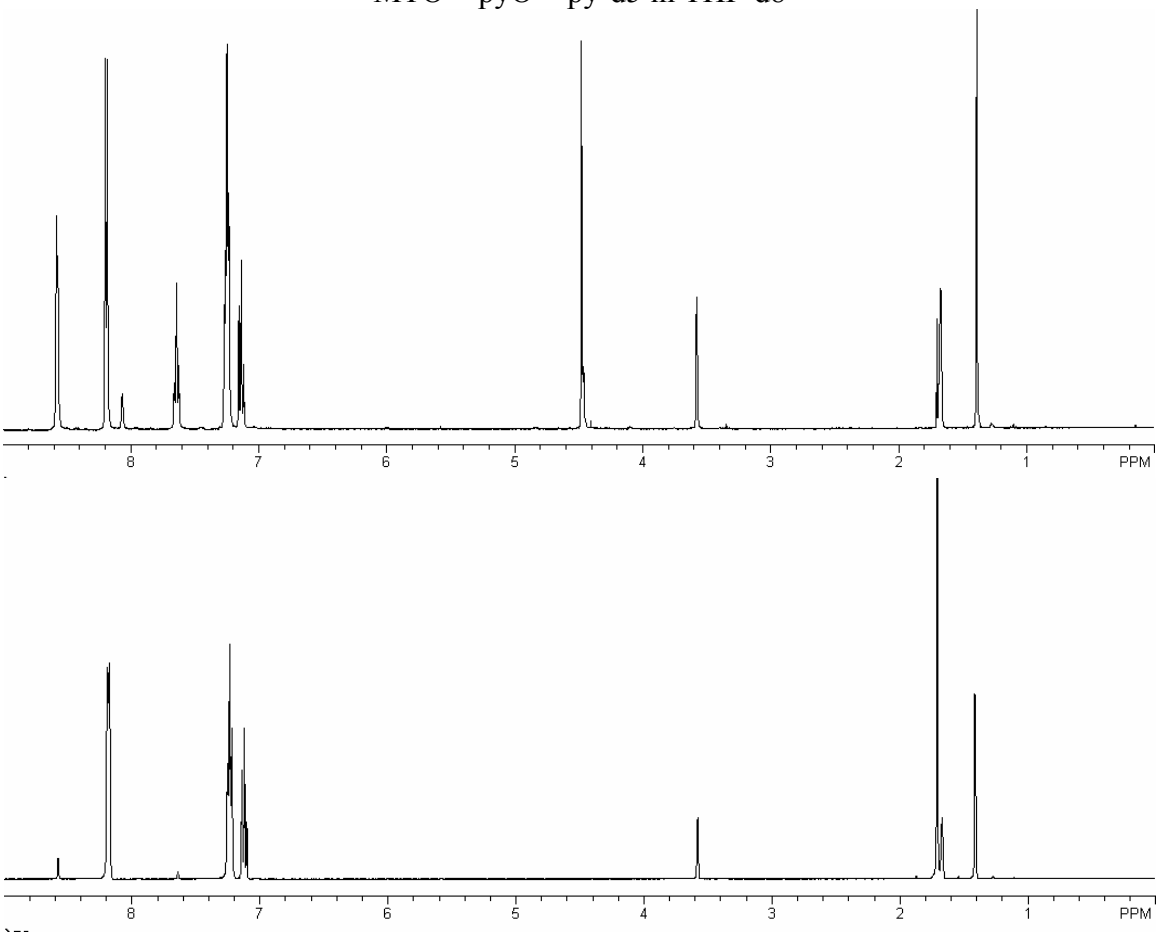

Figure 1: ^{1}H NMR (py_{d5}/THF_{d8}) of MTO + pyO reaction at **t=0** (bottom) and **t=1h** (top): δ 3.58 and δ 1.67 (residual THF resonances); δ 8.19 (d, 2H, *o*-pyO); δ 7.25 (m, overlapping *m*-pyO and $pyridine_{h5}$); δ 7.12 (t, 1H, *p*-pyO); δ 8.58 (d, 2H, $pyridine_{h5}$); δ 7.65 (t, 1H, $pyridine_{h5}$); δ 4.48 (s, C*H*$_3$O-Re); δ1.70 (s, 3H, MTO methyl); δ 1.40 (cyclohexane I.S.).

MTO + YO + D_2O ⟶ CH_3OH: All reactions were carried out under air in D_2O in 8" J-Young NMR tubes. Approximately 16 mg (0.067 mmol) MTO was dissolved in D_2O with the aid of sonication. 2 equivalents of YO were added and allowed to react for 1-1.5 hours. The reaction with OsO_4 required 2 equivalents of KOD to produce methanol and thus is reported in Table 1 as Os O_4 $(OH)_2^{2-}$. All appropriate blanks were taken to assign solvent peaks, oxidant peaks, and product (methanol) formation. NMR spectra were obtained on a Varian Mercury 400 spectrometer (400.151 MHz for ^{1}H). Chemical shifts are given in ppm relative to residual solvent proton resonances (D_2O at 4.79 ppm). Cyclohexane (5 μL in 2mL CCl_4) was used as an external standard. All reactions were carried out under air at room temperature.

MTO + D_2O

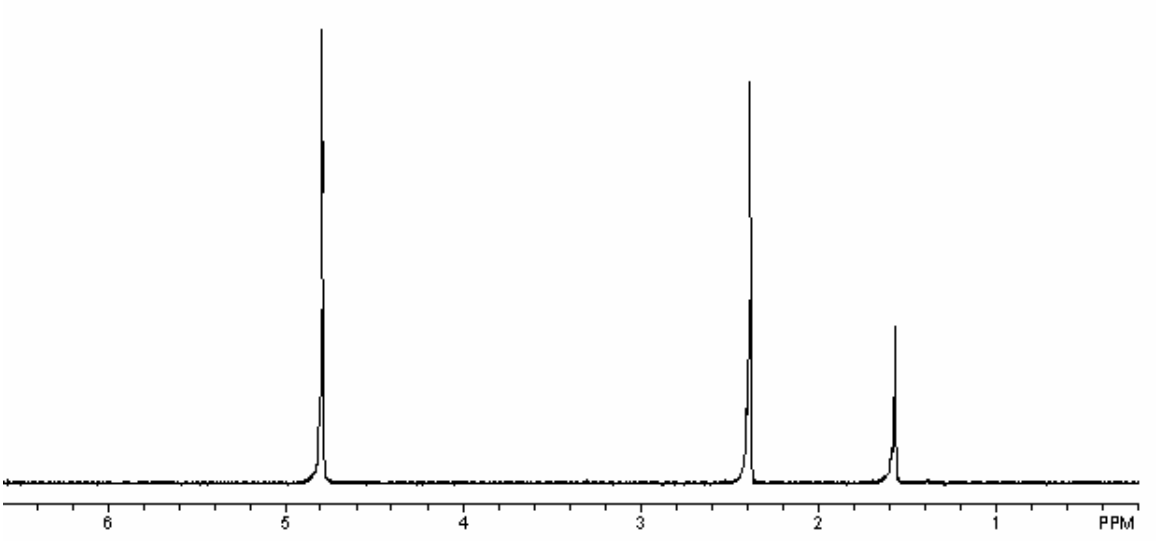

Figure 2: ^{1}H NMR of MTO in D_2O with cyclohexane internal standard. δ 2.38 (s, 3H, MTO methyl); δ1.57 (s, cyclohexane I.S.); δ 4.79 (H_2O residual peak).

MTO + H_2O_2 + D_2O

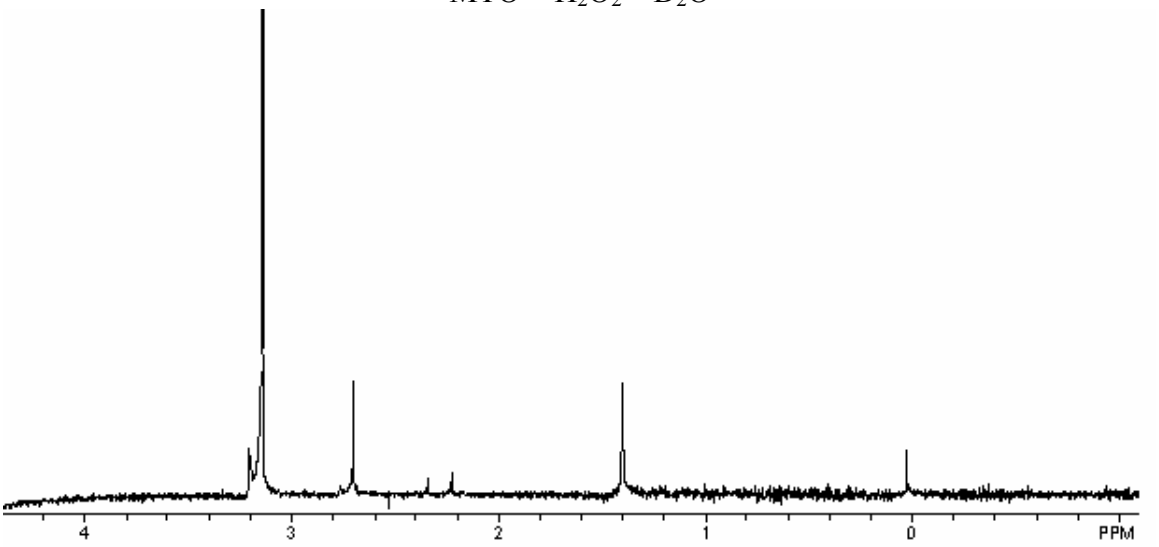

Figure 3: ^{1}H NMR of MTO + H_2O_2 in D_2O with cyclohexane internal standard: δ 2.70 (s, 3H, MTO methyl); δ1.40 (s, cyclohexane I.S.); 3.14 (s, 3H, methanol).

MTO + PhIO + D_2O

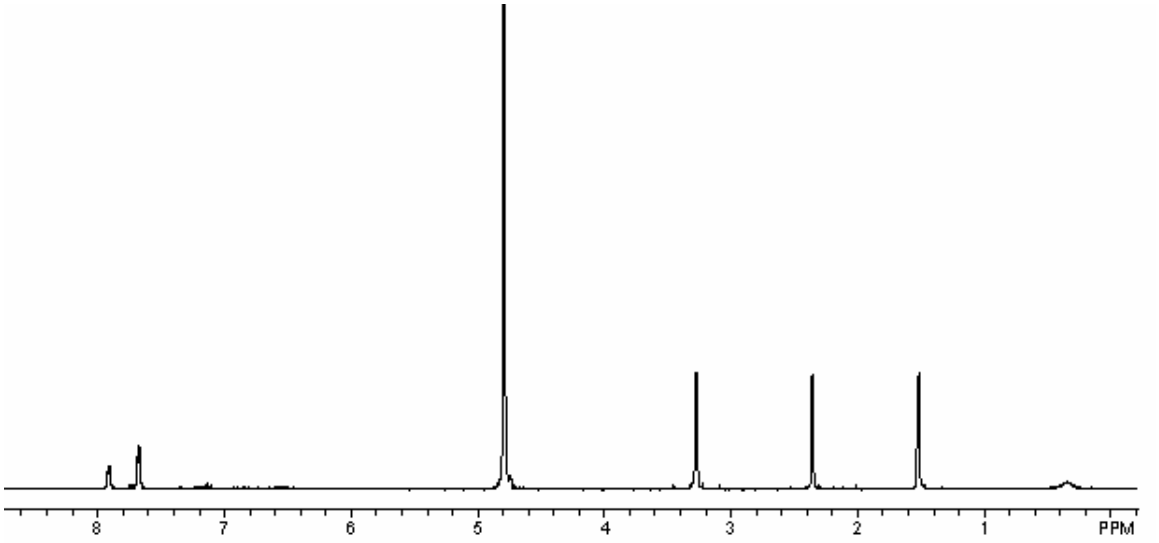

Figure 4: ^{1}H NMR of MTO + PhIO in D_2O with cyclohexane internal standard: δ 1.52 (cyclohexane); δ 2.36 (s, 3H, MTO methyl); δ 3.28 (s, 3H, methanol); δ 4.79 (H_2O residual peak).

MTO + OsO_4 + KOD + D_2O

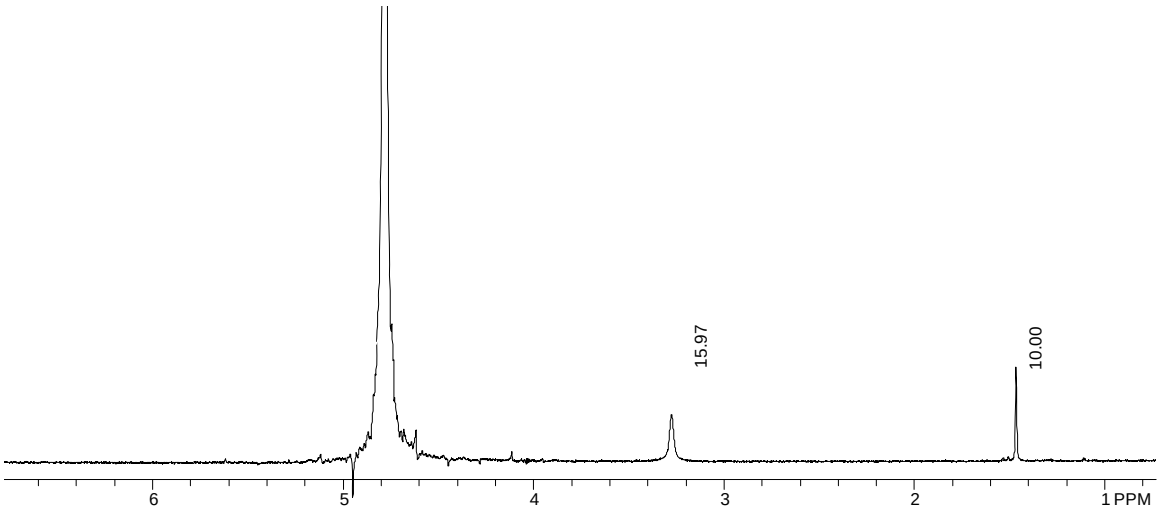

Figure 5: ^{1}H NMR of MTO + OsO_4 in D_2O with added KOD and cyclohexane internal standard: δ 1.47 (cyclohexane); δ 3.28 (s, 3H, methanol); δ 4.79 (H_2O residual peak).

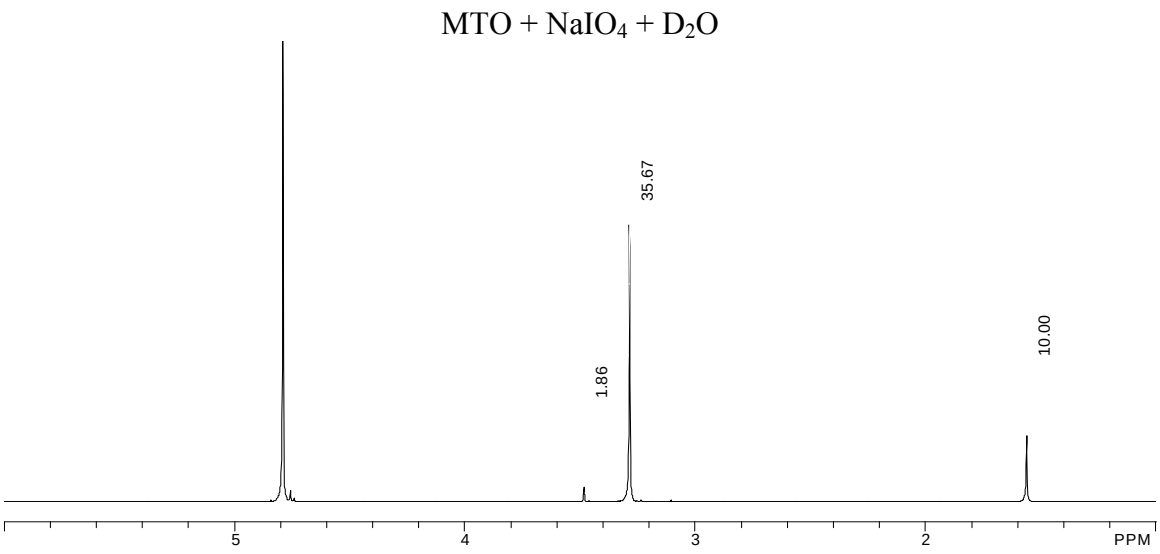

Figure 6: ^{1}H NMR of MTO + $NaIO_4$ in D_2O with cyclohexane internal standard: δ 1.56 (cyclohexane); δ 3.28 (s, 3H, methanol); δ 4.79 (H_2O residual peak).

Theoretical Considerations: All theoretical calculations were performed with the B3LYP[2,3] density functional, in combination with the Jaguar 6.0[4] computational package. Rhenium and osmium were described with the effective core potential of Hay and Wadt[5], iodine with the effective core potentials of Ermler and colleagues[6] while all other atoms used the 6-31G**[7] all electron basis set. The effects of diffuse functions (namely 6-31G**++) were included with single point calculations. Solvation effects, in water, (computed via single point corrections) were modeled implicitly with the PCM[8,9] model ($\varepsilon = 80.37$, $r_{solv} = 1.4$).

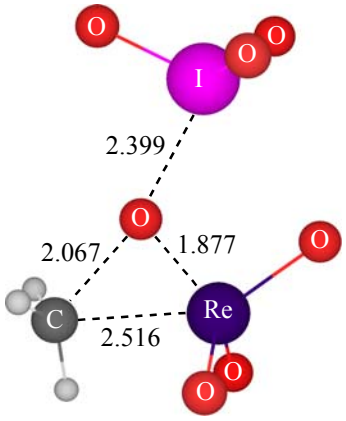

Figure 7: . B3LYP/LACVP/6-311G** BV-type Transition State for MTO + IO_4^-.

As shown in Figure 7, the BV-type transition state involves concerted methyl migration and IO_3^- loss as observed by stretching of the C-Re bond from 2.168 Å to 2.516 Å and the I-O bond from 1.803 Å to 2.399 Å

Cartesian coordinates, enthalpies of key reactants, intermediates and products:

MTO: Enthalpy -344.735079

Re	0.0225076773	-0.0389976943	0.9841137885
O	-0.0412669306	0.0721630199	-0.7188448601
O	-0.8650944722	-1.3564082344	1.6111155616
O	1.6068674707	0.0713482115	1.6119648144
C	-0.9620317510	1.6659935371	1.6802485195
H	-0.4377146603	2.5502800084	1.3083854987
H	-0.9545215728	1.6546922393	2.7734008924
H	-1.9904965715	1.6534915104	1.3097371021

OOH- reaction

HOOH: Enthalpy -151.524452

H	-1.0954082085	-0.5181115430	-0.1127101386
O	-0.6955460318	0.2156509838	0.3804764064
O	0.6951350748	-0.2155547136	0.3803823417
H	1.0951998361	0.5183769146	-0.1123842364

OOH-: Enthalpy -151.094175

O	-0.7310552170	0.2271846813	0.3801763264
O	0.7306760620	-0.2271883720	0.3807340958
H	1.0946951166	0.5199633660	-0.1132043404

OH-: Enthalpy -75.971064

O	0.7302746777	-0.2280123124	0.3812787519
H	1.1010653770	0.5330398984	-0.1218484279

Complex: Enthalpy -495.832953

Re	0.0298271438	-0.0255134190	0.9853726224
O	0.7791697496	0.6990804187	-0.4016481557
O	-0.3480621300	-1.6513396528	0.3984820841
O	1.1841411740	-0.0772697496	2.2620460995
C	-0.9084243165	1.9526485893	1.2227400199
H	-0.0950584448	2.6837576753	1.2000729724
H	-1.4685507152	2.0070682718	2.1550157327
H	-1.5740067000	2.1296874465	0.3744139270
O	-1.7823399141	-0.2282879115	1.8730081936
O	-2.2045452262	-1.6020674937	2.1093129530
H	-1.6651819166	-2.0383345475	1.4026224542

Baeyer-Villager Transiton State: Enthalpy -495.800542

Re	0.0925144043	0.0569160102	-0.0015241948
O	-0.5923406510	-0.4016474321	1.5326356769
O	1.6806269868	0.5655635261	0.4701284185
O	0.0984742678	-1.4222616653	-0.8890690619
C	-2.1595823735	1.2856073095	0.0884650738
H	-2.6995686603	0.3396596418	0.0882243655
H	-2.5725467561	2.0002569508	-0.6169751156
H	-2.0270673552	1.6830849346	1.0914193806
O	-0.5029402316	1.4013033038	-1.1387515027
O	0.9672094661	1.1653969133	-2.2162263003
H	1.5574174855	1.7306991857	-1.6926802475

Product: Enthalpy -419.958234

Re	0.0960135290	-0.0252090513	0.0083133782
O	0.3207157605	0.3447293605	1.6623250847
O	1.5749838015	0.0830802637	-0.8394712242

O	-0.5557180356	-1.6010380673	-0.1149101093
C	-2.4434719506	1.4583523647	-0.3570414263
H	-3.0467614877	0.5509411150	-0.4585325560
H	-2.8165460393	2.2307213282	-1.0323814459
H	-2.4762597794	1.8177760364	0.6760502544
O	-1.0845566309	1.1937849604	-0.7443093694

PyO reaction

PyO: Enthalpy -323.379837

C	-1.2453415647	-0.1912252723	0.0002757594
C	0.1376857259	-0.2051196657	0.0002519491
C	0.8606448469	0.9894878081	-0.0004860143
C	0.1377958141	2.1841618802	-0.0011930686
C	-1.2452333159	2.1703967678	-0.0011578157
H	-1.8754819987	-1.0700577673	0.0008263226
H	0.6412578248	-1.1663931709	0.0008209650
H	1.9444614065	0.9894369751	-0.0005091501
H	0.6414583301	3.1453876167	-0.0017836474
H	-1.8752944511	3.0492868349	-0.0016814267
N	-1.9494849913	0.9896184123	-0.0004258756
O	-3.2228763298	0.9896770390	-0.0003983688

Py: Enthalpy -248.209568

C	-1.2692437223	-0.1526414456	0.0002607430
C	0.1256196330	-0.2088805465	0.0002601027
C	0.8378780829	0.9895048952	-0.0004872800
C	0.1257009862	2.1879409818	-0.0011950523
C	-1.2691601068	2.1318083715	-0.0011244425
H	-1.8544479484	-1.0711281496	0.0008267178
H	0.6355253817	-1.1673526370	0.0008236424
H	1.9243557612	0.9894656194	-0.0005195675
H	0.6357047258	3.1463601195	-0.0017910419
H	-1.8542958606	3.0503385868	-0.0016694354
N	-1.9675430946	0.9896093263	-0.0004161403

Complex: Enthalpy -668.115827

Re	-0.0283353162	-0.0733140427	-0.0126672563
O	1.4077973818	-0.4457883853	1.9559748106
O	-0.7203858684	0.2978608126	-1.5312043221
O	-0.7834254794	0.9500135419	1.1442046657
O	-0.2262522282	-1.7643207189	0.2258446822
C	1.9263645389	0.5164038542	-0.5679251586
H	2.2238926494	-0.1000125853	-1.4215845614
H	2.6153896524	0.3921580538	0.2645744965
H	1.8761728020	1.5615871146	-0.8872520501
C	0.6231529854	-2.2762308891	3.1280073772
C	0.1722926673	-0.0791814816	3.8739393289
C	-0.0610522622	-2.8035256214	4.2104016616
H	1.0879725743	-2.8538759817	2.3421701342
C	-0.5185736486	-0.5730646916	4.9676506634
H	0.3039801788	0.9672102254	3.6396881816
C	-0.6412627991	-1.9510336707	5.1505502790
H	-0.1355977339	-3.8811732038	4.3030774794
H	-0.9587811770	0.1306185122	5.6650911409
H	-1.1793041601	-2.3507619180	6.0029450169
N	0.7395875377	-0.9297256451	2.9773588070

Baeyer-Villager Transition State: Enthalpy -668.064204

Re	-0.0085348126	0.0290036580	0.0706414122
O	0.0152669732	-0.1380269548	2.0014431810
C	1.9750188822	0.3546044552	1.3422552660
N	-1.5421420243	-0.5486446055	2.7296410086
O	0.7883687521	-1.1709062413	-0.8638872680
O	0.1659723515	1.5967691918	-0.6076644779
O	-1.6997419577	-0.3533622093	0.0939073618
H	2.3407366463	-0.5453400860	1.8238346055
H	1.9467833083	1.2239316601	1.9894633639
H	2.4972231267	0.5587852592	0.4035031909
C	-1.7614126666	-1.8240817633	3.0400960969
C	-2.3245601959	0.4412178904	3.1539240251
C	-2.8543185891	-2.1734085416	3.8286732307
H	-1.0565287764	-2.5456265183	2.6421944871
C	-3.4351880055	0.1629536311	3.9457465962
H	-2.0497801776	1.4425878913	2.8418922604
C	-3.7016736746	-1.1637613004	4.2868974195
H	-3.0307278051	-3.2152588015	4.0718550242
H	-4.0729902378	0.9733119815	4.2809354368
H	-4.5609087832	-1.4081642203	4.9029513384

mu-peroxo Transition State: Enthalpy -668.040308

Re	0.0624229735	0.0929855350	0.1148554018
O	0.0933715171	-0.8053029649	1.6800524689
O	1.7356600616	-0.6198029599	1.0061822269
N	3.4699882358	-0.4453954372	0.3691885905
O	-0.8991264370	-0.7929565791	-0.9828237174
O	-0.5891737295	1.6434640809	0.4071879039
C	1.4478843099	0.7658959342	-1.3833084208
H	0.8075840941	1.2646379865	-2.1159161738
H	1.9623377373	-0.0716671894	-1.8531111502
H	2.1671784651	1.4753709839	-0.9766532877
C	4.0111083681	-1.4772025588	-0.2791437339
C	4.2270085764	0.4976189804	0.9307649587
C	5.3923698382	-1.5870294166	-0.4256780056
H	3.3179013542	-2.2132616043	-0.6740860070
C	5.6157507994	0.4583647350	0.8272943445
H	3.6986644502	1.2792150484	1.4674375639
C	6.2052414845	-0.6013006229	0.1362000026
H	5.8141786307	-2.4296661764	-0.9626928985
H	6.2145620006	1.2383136356	1.2849218171
H	7.2849767733	-0.6620723931	0.0430527563

Product: Enthalpy -419.958234
Structure same as OOH- product.

$OsO_4(OH)_2$ 2- reaction

$OsO_4(OH)_2$ 2-: Enthalpy -543.844876

Os	-.7463601841	.5996390240	.0220807569
O	-.6297925986	.8612937756	-1.7545424958
O	-.5140290157	.9496556223	1.7507418610
O	1.4084831676	.7196888233	-.0424524674
O	-2.5184996218	.7418718424	.0729898417
O	-.4173134208	2.7257489839	-.0606387923
H	-.3961198167	2.7749937926	-1.0284129814
O	-.5081916368	-1.1459760199	.0386679090
H	1.4301970630	1.6794716188	.0852666098

$OsO_3(OH)_2$ 2-: Enthalpy -468.678315

Os	-0.6800897024	0.6036357758	-0.2154875116
O	-0.6867707813	0.9177779333	-2.0469159141
O	1.0045949161	0.4465539125	0.3278899252
O	-2.3074547253	0.3881589607	0.3983453198
O	-0.7064490213	2.6136383155	-0.2956766425
H	-0.7235324690	2.5817253744	-1.2869006799
O	-0.5918666638	-1.5448786697	-0.1472690360
H	0.3573656361	-1.5983342796	0.0321032505

Baeyer-Villager Transition State: Enthalpy -888.535100

Re	-0.0679018512	-0.0504989697	0.0491186282
O	-1.1661509952	0.2845631083	1.3572655921
O	1.5536482973	0.2618675710	0.5659091221
O	-0.2920779592	-1.7171014441	-0.3663564932
O	-0.5029519405	0.6791722341	-1.6405316166
C	-0.4280215210	2.3559017877	-0.7510603283
H	0.3784023031	2.5597075128	-0.0439644813
H	-1.4298894510	2.4671110911	-0.3536192953
H	-0.2321923847	2.7727258127	-1.7527673699
O	1.5386925389	0.0243279766	-3.1813083495
Os	0.0936552365	0.7539663525	-3.8256342204
O	0.3096046346	0.6245031188	-5.5951423264
O	0.3646530192	2.5111691359	-3.5773314371
O	-0.8936976645	-1.0567443452	-4.1418379973
O	-1.8683336839	1.2808223528	-3.7973694830
H	-0.7470991948	-1.1105735630	-5.1023517755
H	-2.2291477106	0.3787269243	-3.8195317207

Product: Enthalpy -419.958234
Structure same as OOH- product

IO_4- Reaction

IO_4-: Enthalpy -412.288013

I	-0.3488049918	0.3729442403	-0.0095806512
O	0.2665189166	1.2826546404	-1.4392713358

O	-2.1499153212	0.3142055189	-0.0638167927
O	0.3080813504	-1.3057771050	-0.0372813961
O	0.1800028342	1.2006511465	1.5022063895

IO_3-: Enthalpy -337.145366

I	-0.3391880367	0.3879665852	0.0178202602
O	0.2618689636	1.2755533045	-1.4573055975
O	-2.1582312765	0.3057806960	-0.0796754760
O	0.3038257539	-1.3169447465	-0.0528848218

Baeyer-Villager Transition State: Enthalpy -756.996419

Re	0.0125788072	-0.0317477788	0.0160164527
O	-0.0534120389	0.0082720311	1.7367133655
O	1.6598328991	-0.1326246661	-0.4891221793
O	-0.2777119564	1.6046665450	-0.8558098364
O	-0.8569993435	-1.3820537344	-0.6062302405
C	-2.1375939174	1.2733802799	-0.0180711596
H	-2.5734694769	1.3251801555	-1.0070006458
H	-2.0523133382	2.2126597196	0.5122241572
H	-2.5058240134	0.4462201087	0.5910786957
I	1.5805998896	2.5405607427	-2.0508271140
O	0.6240116586	3.9792654094	-2.5811742513
O	2.9926767633	3.1222770178	-1.0773436265
O	2.1546598663	1.6623581215	-3.5269952758

mu-peroxo Transition State: Enthalpy -756.964939

Re	-0.0589378784	0.0003845822	-0.0153604521
O	-0.0604775362	-0.0022140352	1.8322308989
O	1.4627757478	-0.0001385500	1.2554496647
I	4.0502734276	0.0033312041	0.6251010514
O	-0.8314905435	-1.4173712439	-0.5710615777
O	-0.8317733230	1.4192945439	-0.5675807072
C	1.4823839491	0.0021137889	-1.4815235915
H	0.9351553858	0.0026515109	-2.4289955277
H	2.1043224281	-0.8905829802	-1.3863569759
H	2.1037130463	0.8951104476	-1.3850593024
O	4.3726874336	1.4736518689	-0.3998671866
O	4.3757652622	-1.4666957526	-0.3993406744
O	5.2069415444	0.0047727063	2.0230808793

Product: Enthalpy -419.958234
Structure same as OOH- product

PhIO Reaction

PhIO: Enthalpy -418.142340

C	-2.5331172743	0.6144599249	-0.0617961204
C	-1.1508928402	0.4238865499	0.0188825993
C	-0.3281927309	1.5423128353	-0.0580449172
C	-0.8229275879	2.8318810894	-0.2098995559
C	-2.2074217087	3.0039132056	-0.2874632030
C	-3.0591784144	1.8991978279	-0.2150230612
H	-3.1948234494	-0.2451974248	-0.0046737500
H	-0.7415038221	-0.5757123678	0.1385802180

H	-0.1282214064	3.6684160667	-0.2648751230
H	-2.6193820817	4.0021358626	-0.4067247953
H	-4.1347945506	2.0377465035	-0.2785718398
I	1.8245299593	1.4062976055	0.0495021421
O	2.2937770171	3.2194862384	-0.1044916291

PhI: Enthalpy -343.019569

C	-2.5292103574	0.4387685805	0.0002127487
C	-1.1325406835	0.4307501315	0.0006156919
C	-0.4460895929	1.6459698872	0.0001828524
C	-1.1324470471	2.8612315692	-0.0008902187
C	-2.5291042359	2.8533199227	-0.0013423806
C	-3.2292367927	1.6460730597	-0.0007603293
H	-3.0659632985	-0.5056010328	0.0006343804
H	-0.5907046282	-0.5088195556	0.0015881560
H	-0.5905197053	3.8007512670	-0.0012188136
H	-3.0658097355	3.7977169249	-0.0020932946
H	-4.3149104335	1.6461455571	-0.0011219934
I	1.6964303864	1.6458386763	0.0010554152

Complex: Enthalpy -762.887453

Re	-0.1136171847	0.4606042883	0.1380386389
O	0.5058859271	1.7311349611	1.0961640391
O	1.2909028156	-0.2260926545	-0.7856905771
O	-0.6631263436	0.7473893459	-1.7681078828
O	-0.7402017034	-0.8136438972	1.0868680222
C	-2.0933796894	1.4263069046	0.0046520384
H	-2.3377318370	1.5405749261	1.0635471986
H	-2.7932665673	0.7682192360	-0.5031437142
H	-2.0072398468	2.3872440922	-0.4952721889
I	0.7993732932	0.0461318866	-3.0098384667
C	-0.4829214991	0.6315260344	-4.6334598857
C	-0.7830409384	-0.3104461790	-5.6198199055
C	-0.9684944832	1.9395046896	-4.7147336214
C	-1.5620266745	0.0709753652	-6.7155734697
H	-0.4239349490	-1.3325619932	-5.5405545969
C	-1.7572755032	2.3051093347	-5.8054544506
H	-0.7454893768	2.6584664387	-3.9336367488
C	-2.0490663644	1.3749477150	-6.8068596198
H	-1.7958816839	-0.6564039256	-7.4871695551
H	-2.1414783569	3.3185352679	-5.8740312189
H	-2.6599089608	1.6666933405	-7.6556996266

Baeyer-Villager Transition State: Enthalpy -762.874390

Re	0.1928708004	-0.3016777024	-0.1767187369
O	1.2324198720	-0.0915942402	1.1717919619
O	1.1859973200	-0.6631682246	-1.6018958902
O	-0.3122450370	1.2296488538	-1.2103682050
O	-0.9330497395	-1.5781150108	0.0382282749
C	-1.3342839207	1.1717809747	0.7972955940
H	-1.3972332617	0.5734052067	1.7073742463
H	-2.2490982693	1.1870079151	0.2184230210
H	-0.8725836605	2.1406404103	0.9409032974
I	0.7070655384	1.2589495901	-3.1826753009
C	2.1258169685	0.1038501647	-4.3062640134
C	3.4829110640	0.4190794980	-4.2153636526
C	1.6698503945	-0.9255194031	-5.1319401307
C	4.3955591990	-0.2954766034	-4.9929376951
H	3.8277364368	1.2064198292	-3.5535152776
C	2.5946764567	-1.6307259071	-5.9031531558
H	0.6154646024	-1.1758761520	-5.1777396137
C	3.9532498600	-1.3172197919	-5.8346208443
H	5.4525955962	-0.0543002916	-4.9333553385
H	2.2498548448	-2.4290131201	-6.5534465535
H	4.6680395888	-1.8732857721	-6.4333489646

Mu-Peroxo Transition State: Enthalpy -762.852895

Re	0.1584963588	-0.2252561677	-0.1977264655
O	-0.1422985097	-1.0079163833	1.3711162699
O	1.6689188727	-0.3106101807	1.2637376383
I	3.6779057475	0.4708184523	1.4887971073
O	0.3771228085	-1.4022153266	-1.4113658015
O	-1.2543164580	0.6843723125	-0.5148702239
C	1.4041575765	1.3367334722	-1.0000491578
H	0.8946450388	1.6255793919	-1.9229438528
H	2.4079369344	0.9865978592	-1.2351172339
H	1.4418331457	2.1919274924	-0.3232835593
C	5.0423828702	0.1064738130	-0.1102023200
C	5.3651931145	1.1490852195	-0.9835150809
C	5.5878953056	-1.1717226021	-0.2584899177
C	6.2779005748	0.9052092917	-2.0111095601
H	4.9229582047	2.1323865208	-0.8641837528
C	6.4942530555	-1.3980249011	-1.2943774231
H	5.3148756749	-1.9733377042	0.4190564664
C	6.8407169348	-0.3628538256	-2.1653350169
H	6.5436280034	1.7091924337	-2.6899905213
H	6.9272379163	-2.3854653869	-1.4180050302
H	7.5484394447	-0.5459736273	-2.9675012243

Product: Enthalpy -762.875227
Product Structure Same as OOH- case

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